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14. ABSTRACT Numerous examples can be found in nature of microorganisms that assemble oxide nanoparticles into rigid (bioclastic) microstructures with intricate, but well-controlled 3-D shapes and fine (nanoscale) features. Because such self-assembly is under genetic control, a given microorganism can generate bioclastic replicas with a high degree of fidelity upon biological reproduction. Continuous reproduction (repeated doubling) of such micro-organisms can yield enormous numbers of identically-shaped bioclastic structures. Such genetically-precise and massively-parallel self-assembly is a highly-attractive means of generating large quantities of ceramic particles with complex and well-defined shapes. However, natural bioclastic compositions (amorphous SiO <sub>2</sub> , CaCO <sub>3</sub> ) are not well-suited for high-temperature applications. This research has been focused on the shape-preserving chemical conversion of natural, bioclastic structures (diatom microshells) into refractory ceramics					
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## **AFOSR Final Performance Report**

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## REACTIVE CONVERSION OF BIOCLASTIC NANOSTRUCTURES

AFOSR GRANT NUMBER F49620-03-1-0182

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### Abstract

Numerous examples can be found in nature of microorganisms that assemble oxide nanoparticles into rigid (bioclastic) microstructures with intricate, but well-controlled 3-D shapes and fine (nanoscale) features. Because such self-assembly is under genetic control, a given microorganism can generate bioclastic replicas with a high degree of fidelity upon biological reproduction. Continuous reproduction (repeated doubling) of such micro-organisms can yield enormous numbers of identically-shaped bioclastic structures. Such genetically-precise and massively-parallel self-assembly is a highly-attractive means of generating large quantities of ceramic particles with complex and well-defined shapes. However, natural bioclastic compositions (amorphous  $\text{SiO}_2$ ,  $\text{CaCO}_3$ ) are not well-suited for high-temperature applications. This research is focused on the shape-preserving chemical conversion of natural, bioclastic structures into alumina and other refractory ceramics.

### Research Objective

The objectives of this research are: i) to develop methods for converting nanoparticle-based bioclastic assemblies into other, refractory ceramics while preserving the intricate 3-D morphologies of these structures, and ii) to develop a better understanding of the transformation mechanisms associated with such shape-preserving chemical conversion.

### Results and Discussion

#### *Bioclastic Preforms: Silica-based Diatom Frustules*

The bioclastic structures utilized in this research are the microshells (frustules) of diatoms (a type of single-celled aquatic algae). Each diatom generates an intricate microscale frustule comprised of a nanoporous assemblage of silica nanoparticles [1-3]. The 3-D shapes and fine features ( $10^2$  nm pores, channels, protuberances) of diatom frustules are species specific [1-3]. Indeed, a spectacular variety of frustule shapes are formed among the various diatom species. The frustules of 30 diatom species are illustrated in Figure 1a below [1]. The co-continuous nature of the pores and silica particles, the aspected shapes, and (in some cases) the intercalating/interlocking features of diatom frustules are among the unique characteristics of these freestanding microstructures that may be exploited in applications.

The frustules of *Aulacoseira* diatoms have been utilized as preforms in this work. Representative secondary electron images of *Aulacoseira* frustules are shown in Figures 1b and 1c. These frustules were cylindrical in shape. The sidewalls of the frustules were decorated with rows of fine pores (several hundred nanometers in diameter). End faces of these frustules

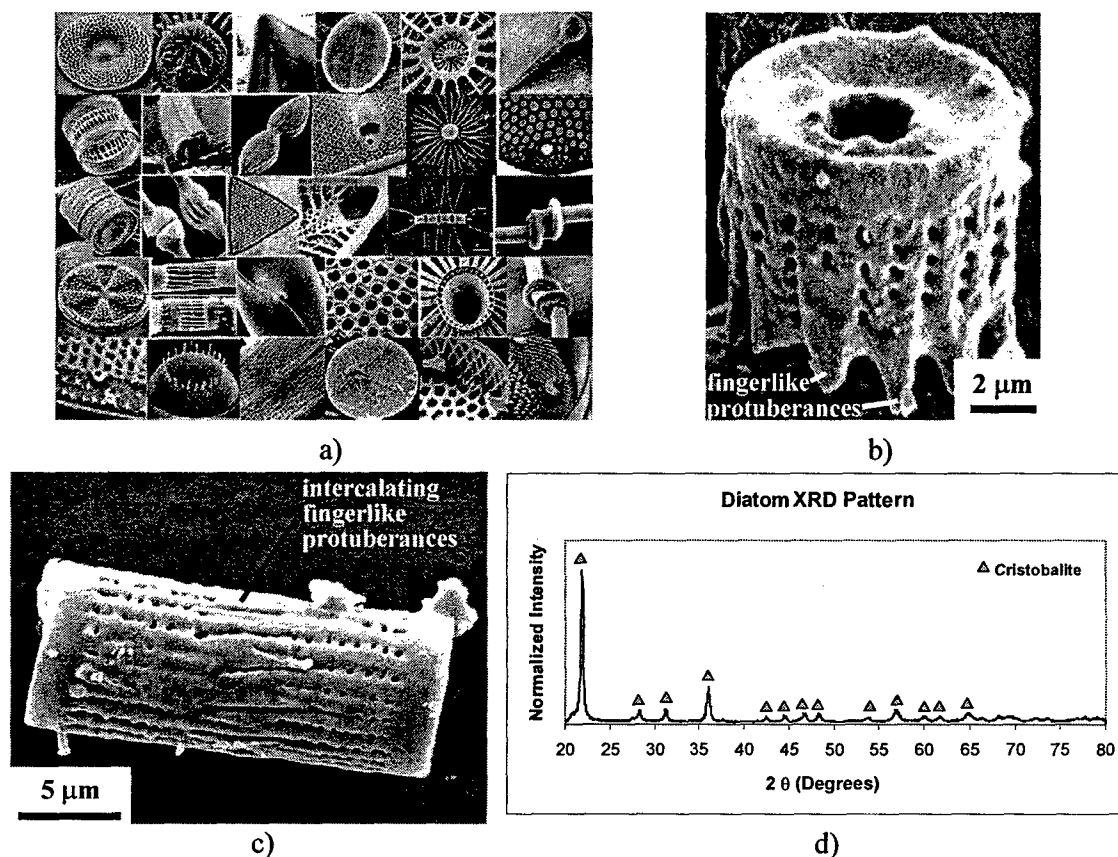
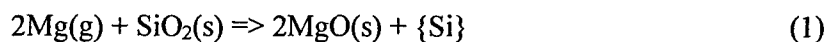


Figure 1. a) Secondary electron (SE) images of  $\text{SiO}_2$ -based microshells (frustules) associated with 30 diatom species (assembled by M. Hildebrand, Univ. California at San Diego, from images in [1]); b), c) SE images of *Aulacoseira* diatom frustules; d) x-ray diffraction (XRD) pattern obtained from the *Aulacoseira* diatom frustules.

possessed a circular hole with a protruding outer rim. The other end of these frustules was closed and possessed finger-like protuberances. The fingerlike protuberances from one cylinder were often observed to intercalate with those of another to form larger, paired assemblies, as is shown in Figure 1c. X-ray diffraction analyses revealed peaks for cristobalite (note: these frustules were obtained as flame-polished diatomaceous earth from a local vendor). Energy-dispersive x-ray (EDX) analyses (not shown) also confirmed the silica-based composition of the starting frustules.

#### **Reactive Conversion into $\text{Al}_2\text{O}_3$ Frustules**

Prior AFOSR-supported research has shown that silica-based diatom frustules can be converted into  $\text{MgO}$ , without losing the frustule shape or features, via the net reaction [4]:



where  $\{\text{Si}\}$  refers to silicon dissolved within a  $\text{Mg-Si}$  liquid (this liquid sweats away from the reacted frustule to yield a  $\text{MgO}$ -based frustule). A secondary electron image of a magnesia-

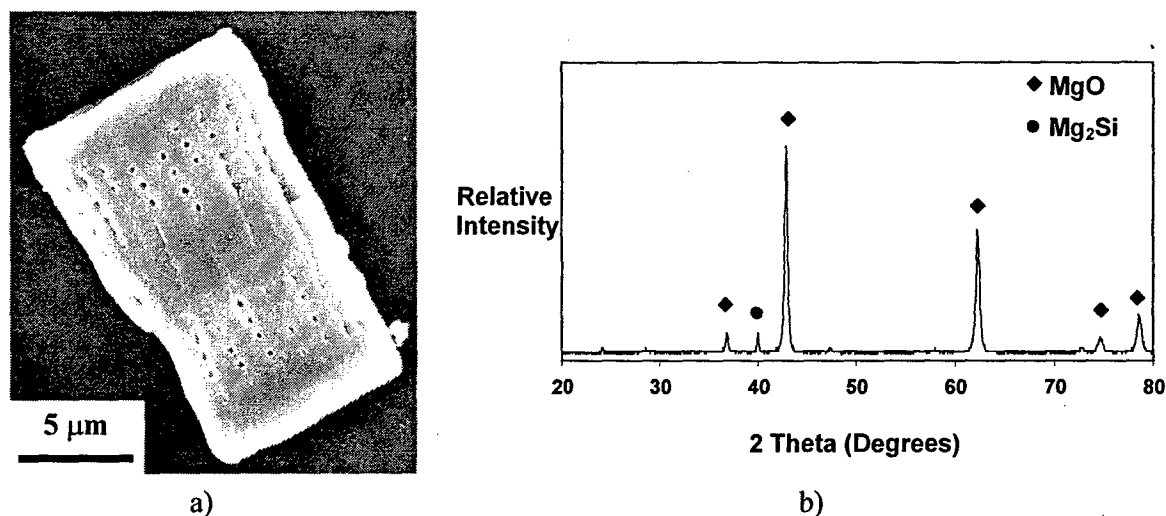
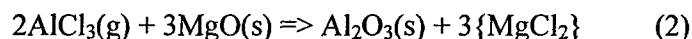


Figure 2. a) A SE image and b) an XRD pattern of MgO-converted *Aulacoseira* frustules generated by the net reaction (1).

converted diatom frustule generated after 1.5 hours of exposure to  $\text{Mg(g)}$  at  $850^\circ\text{C}$  is shown in Figure 2a below. An XRD pattern of such converted MgO frustules is shown in Figure 2b.

The magnesia frustules were then exposed to aluminum chloride vapor to allow for the following net metathetic reaction:



where  $\{\text{MgCl}_2\}$  refers to a magnesium chloride dissolved within a  $\text{MgCl}_2\text{-AlCl}_3$  liquid. Secondary electron images of a magnesia frustule exposed to aluminum chloride vapor at  $700^\circ\text{C}$  for 2 hours are shown in Figures 3a and 3b. An XRD pattern obtained from such reacted magnesia frustules is shown in Figure 3c. The XRD pattern reveals that the magnesia was converted into cubic  $\gamma$ -alumina (the triangular crystallites observed in Fig. 3b are also consistent with this spinel-like polymorph), although some residual magnesia was also retained. The formation of  $\gamma\text{-Al}_2\text{O}_3$  has often been observed to form in advance of the thermodynamically

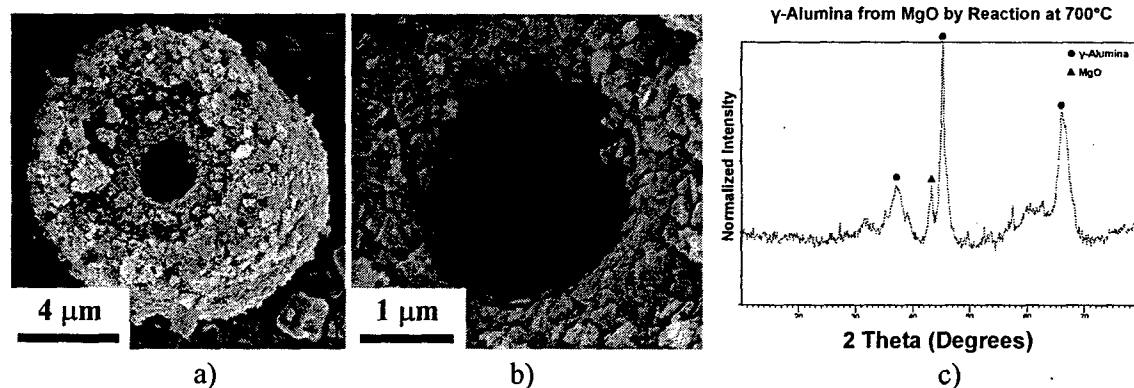


Figure 3. a), b) SE images and c) an XRD pattern of  $\gamma\text{-Al}_2\text{O}_3$ -converted *Aulacoseira* frustules generated by the net displacement reaction (2).

stable  $\alpha$ - $\text{Al}_2\text{O}_3$  (corundum) phase [5,6]. The electron micrograph shows that the nanocrystalline  $\gamma$ -alumina-bearing frustules retained the overall cylinder shape of the starting magnesia frustules. Post-reaction thermal treatments leading to complete conversion of MgO into  $\gamma$ - $\text{Al}_2\text{O}_3$ , as well as for conversion of the metastable  $\gamma$ -alumina polymorph into the more stable corundum phase, are also under investigation. Once optimized reaction conditions are identified for full alumina conversion, then the mechanisms (nanostructural evolution, kinetics) for conversion of magnesia into shape-preserved alumina via reaction (2) will be examined.

### *Homomorphic Coating of Diatom Frustules with $\text{Al}_2\text{O}_3$*

A coating-based approach has also been used to convert silica-based diatom frustules into alumina. *Aulacoseira* diatom frustules were immersed in a solution of aluminum isopropoxide with ethanol, water, and ammonium hydroxide (molar  $\text{EtOH}:\text{Al}(\text{C}_3\text{H}_7\text{O})_3:\text{H}_2\text{O}:\text{NH}_4\text{OH}$  ratio = 1:0.0021:0.0070: 0.0014) for 4.5 hours at 60°C. The solution was then allowed to evaporate for 5 hours at 60°C. The coated frustules were then heated in air at 5°C/min to 800°C and held at this temperature for 2 hours. A secondary electron image of a resulting frustule is shown in Figure 4a. The frustule appears to be largely covered with a coating, as revealed by the presence of a few gaps in the coating on the end face (the presence of an Al-bearing coating was also confirmed by EDX analyses). XRD analysis of such coated frustules (Figure 4b) revealed that the coating was comprised of  $\delta$ - $\text{Al}_2\text{O}_3$ . In an effort to convert the metastable  $\delta$ - $\text{Al}_2\text{O}_3$  coatings into the stable  $\alpha$ - $\text{Al}_2\text{O}_3$  phase, the coated frustules were reheated for an additional 4 hours at 1000°C. An XRD pattern obtained from these specimens is shown in Figure 4c. The coating was again comprised largely of  $\delta$ - $\text{Al}_2\text{O}_3$ .

The as-coated (unfired) frustules were then exposed to microwave heating (via collaboration with Ceralink, Inc., Alfred, NY). The coated specimens were placed inside a SiC susceptor within a 2.45 GHz Thermwave microwave heating system (Research Microwave Systems, Youngstown, NY). The specimens were heated in air within 18 minutes to 1000°C (as evaluated by a thermocouple placed near the coated frustules) and held at this temperature for 5 minutes, after which the microwave was turned off and the specimens were allowed to self cool to room temperature. A secondary electron image and an associated XRD pattern obtained from such microwave processed specimens are shown in Figures 5a and 5b, respectively. XRD analysis indicated that the microwave processed coatings had converted into  $\alpha$ - $\text{Al}_2\text{O}_3$ .

Further work is being conducted to compare the nanostructures (via TEM analyses of cross-sections) of the specimens fired with or without a microwave. The influence of solution coating parameters and conventional (non-microwave) thermal treatments on the formation of homomorphic  $\alpha$ -alumina coatings are also being examined.

Selective removal of the underlying silica from the alumina coatings has also been examined. A secondary electron image of an alumina-coated frustule after exposure to a 10 wt% HF solution for 4 hours at room temperature is shown in Figure 6. An inner and outer alumina coating (due to coating of the inside and outside surfaces of the cylindrical diatom frustules) can be detected in this image, after local removal of the silica located between these layers. It is interesting to note the presence of finely-necked (100-200 nm) bridges in the continuous coating

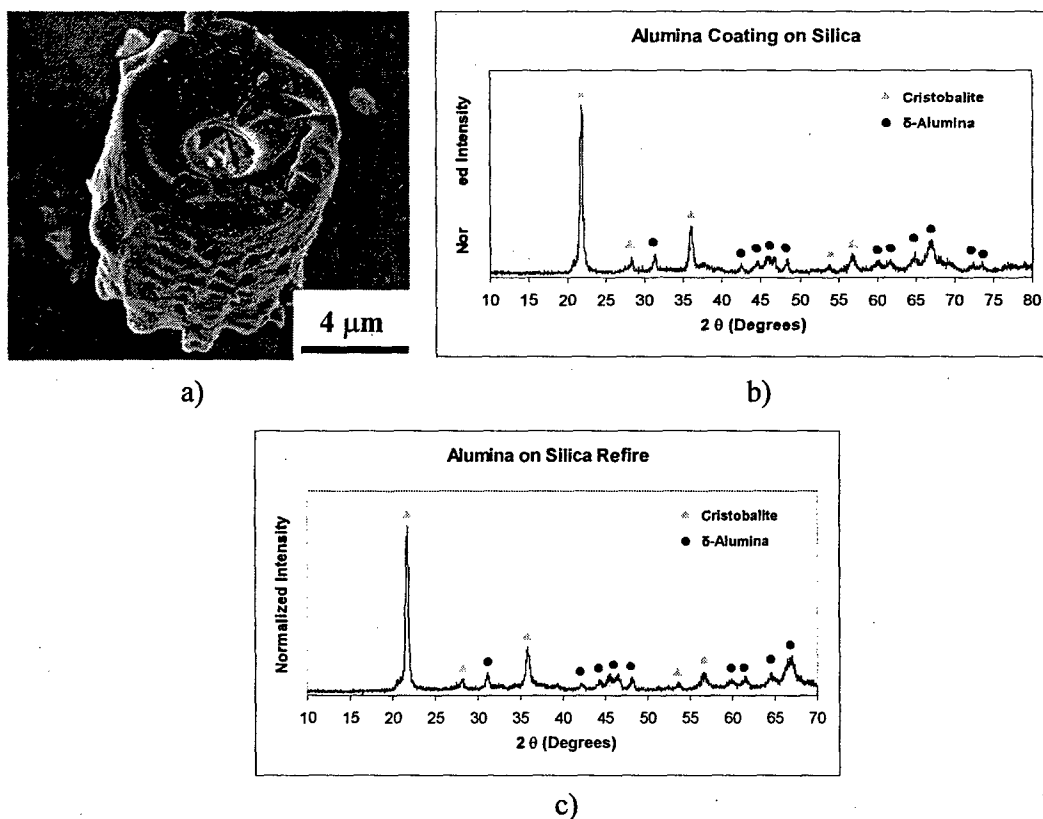


Figure 4. a) A SE image and b) an XRD pattern of  $\delta$ - $\text{Al}_2\text{O}_3$ -coated *Aulacoseira* diatom frustules (after heat treatment at 800°C for 2 hours). C) An XRD pattern revealing the retention of  $\delta$ - $\text{Al}_2\text{O}_3$  in the coating after refiring for 4 more hours at 1000°C.

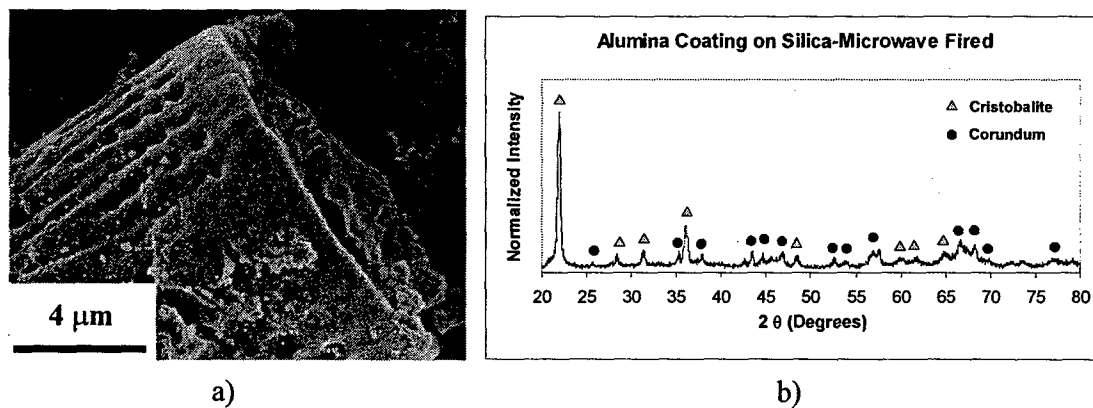


Figure 5. a) A SE image and b) an XRD pattern of  $\alpha$ - $\text{Al}_2\text{O}_3$ -coated *Aulacoseira* diatom frustules (generated via microwave heating).

that survived the dissolution treatment. EDX analysis indicated, however, that some residual silica remained after this acid treatment. Further work is being conducted to identify the conditions required for complete removal of the silica template.

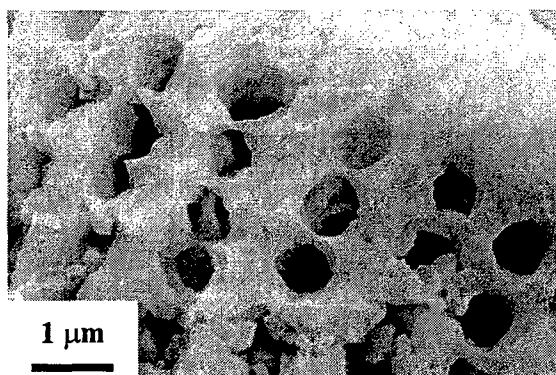


Figure 6. A high-magnification SE image of a  $\delta$ - $\text{Al}_2\text{O}_3$  coating on an *Aulacoseira* frustule after partial dissolution of the underlying silica in a HF solution.

### Summary

Two approaches have been examined for converting self-replicating,  $\text{SiO}_2$ -based bioclastic structures (*Aulacoseira* diatom frustules) into  $\text{Al}_2\text{O}_3$ : i) reactive conversion via a series of gas/solid displacement reactions, and ii) homomorphic coating with a solution containing an alkoxide precursor. With both routes, microscopic transition  $\text{Al}_2\text{O}_3$ -bearing frustules were produced that retained the overall 3-D shape of the starting frustules. Microwave heating was found to enhance the rate of conversion of  $\delta$ - $\text{Al}_2\text{O}_3$  coatings into  $\alpha$ - $\text{Al}_2\text{O}_3$  at  $1000^\circ\text{C}$ .

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